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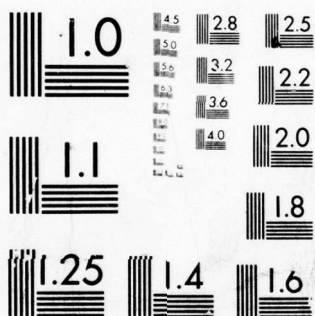
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TECHNICAL REPORT CIVIL ENGINEERING LABORATORY

Naval Construction Battalion Center, Port Hueneme, California 93043

OPERATING COST EVALUATION OF SULFUR DIOXIDE
REMOVAL SYSTEMS FOR BOILER APPLICATIONS

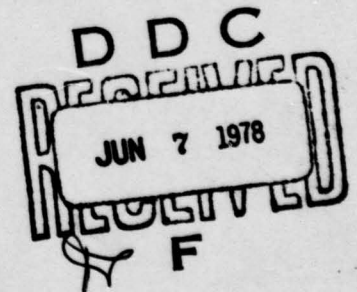
By John M. Slaminski

April 1978

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INTRODUCTION

The Navy currently operates more than 2,000 boilers to provide space heating and process steam for shore facilities. Many of these boilers are obsolete and inefficient, which has led many Navy field activities to consolidate distributed boilers into modern centralized boiler plants. The Navy has been directed to utilize coal in new boiler facilities by the issuance of OPNAVINST 4100.6. Many of the larger Navy boiler plants will be subject to Federal, state, and local emission control regulations, including the removal of sulfur dioxide.

Seven commercial processes for extracting sulfur dioxide from steam or steam-electric generating plants are analytically compared. The operation and economics of lime and limestone slurry scrubbing, dilute and concentrated double alkali, and dilute sulfuric acid processes with gypsum disposal products are contrasted with sodium sulfite/bisulfite and activated char sulfur recovery systems. Each process is critically analyzed to yield system flows and operating expenses (including equipment power consumption, product disposal costs or credits, reagent requirements, and operating and maintenance costs). The laws for scaling these results to any given plant capacity and coal sulfur content are developed and parametrically graphed. This information is a valuable guide for the Navy or utility engineer to perform accurate system evaluations with ease.

BASES FOR COMPARISON

Exhaust Gas Flow Characteristics

Exhaust gas volumetric flow rates from the steam generator are plotted in Figure 1 for conditions at the booster fan discharge prior to entering the absorber or prescrubber, as well as at the absorber exit saturated in water vapor. The predictions are based on combustion calculations described in detail in a previous publication (1) and experimentally verified shortly thereafter (2). The procedure is somewhat lengthy and is beyond the scope of this paper. The predicted flue gas flows correspond to these conditions:

Unit Net Heat Rate	10,546 kJ/kWh (10,000 Btu/kWh)
Air Preheater Volumetric Leakage	10% incoming flow

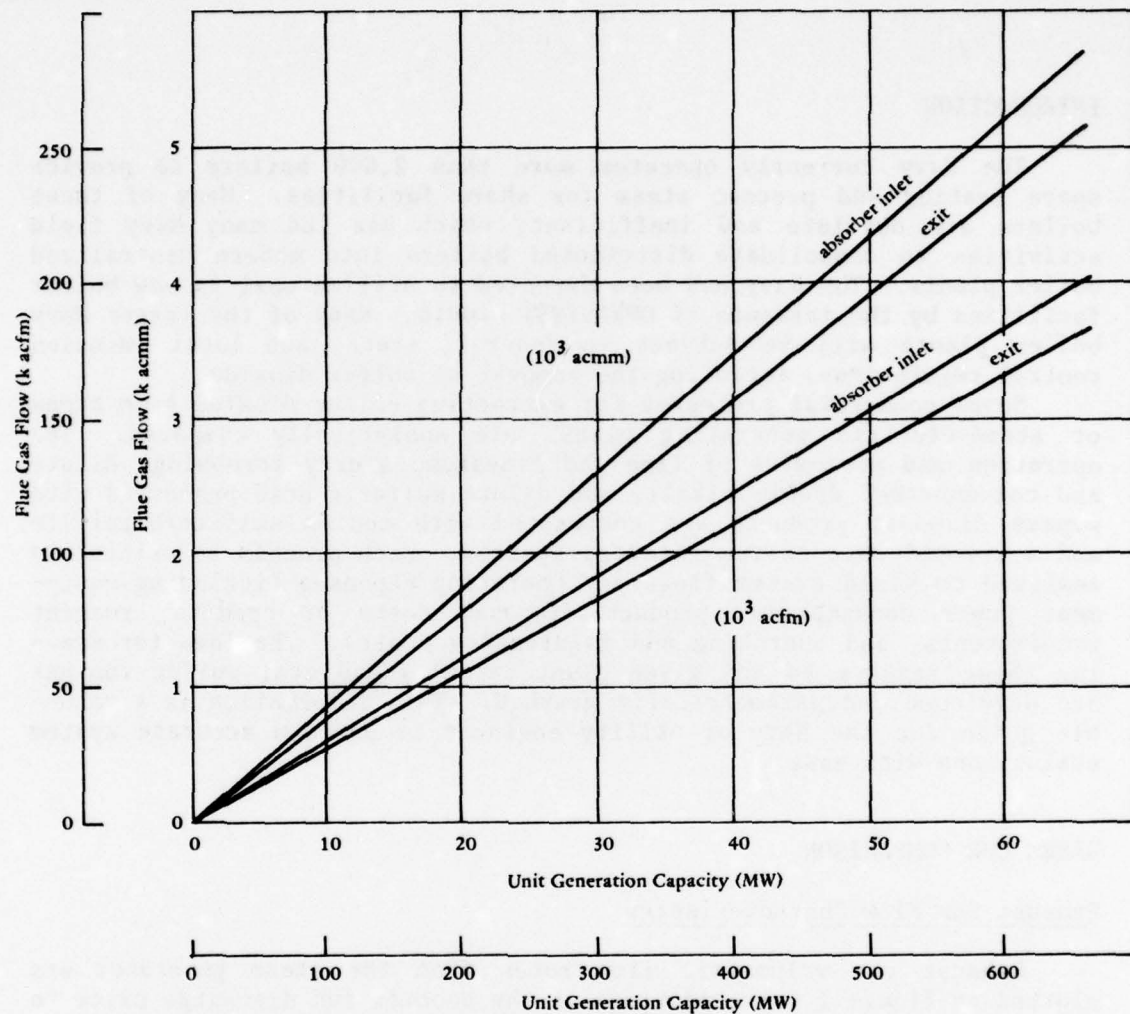


Figure 1. Steam generator exhaust gas volumetric flow rate.
(Multiply flows by 10 for 500 MW capacity.)

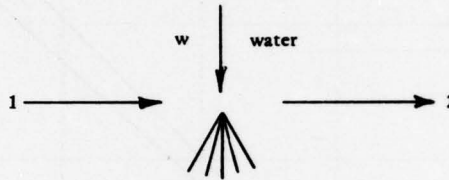
Prescrubber/Absorber Inlet:

Gas Temperature	121C (250F)
Gas Pressure	10.6 Nsca (15.4 psia)
Moisture Content	10% (molar)

Absorber Exit:

Gas Temperature	52C (125F)
Gas Pressure	10.1 Nsca (14.7 psia)
Moisture Content	15% (molar)

The exhaust gas temperature and moisture content were obtained by an iterative solution of the adiabatic humidification, illustrated in the diagram and given in the equation



$$T_1 - T_2 = \frac{m_{w2} - (h_{w2} - h_w) + m_{w1}(h_w - h_{w1})}{C_{pg}/\eta_H} \quad (1)$$

where

$$m_w = m_{w1} - m_{w2}$$

Coal and untreated SO₂ flow rates can easily be computed from

$$\dot{W}_{SO_2} = F_S \dot{W}_F = \frac{HR_N G F_S}{30 HHV} \text{ (kg/min; lb/min)} \quad (2)$$

and were plotted in Figure 2. The removal efficiency of the SO₂ process necessary to meet the Environmental Protection Agency (EPA) standard of performance is shown in Figure 3, indicating that a 90% design efficiency would satisfy this regulation for nearly all coal supplies. The heat rate and coal heating value used throughout this paper are:

Unit Net Heat Rate	10,546 kJ/kWh (10,000 Btu/kWh)
Fuel Higher Heating Value	23,250 kJ/kg (10,000 Btu/lb)

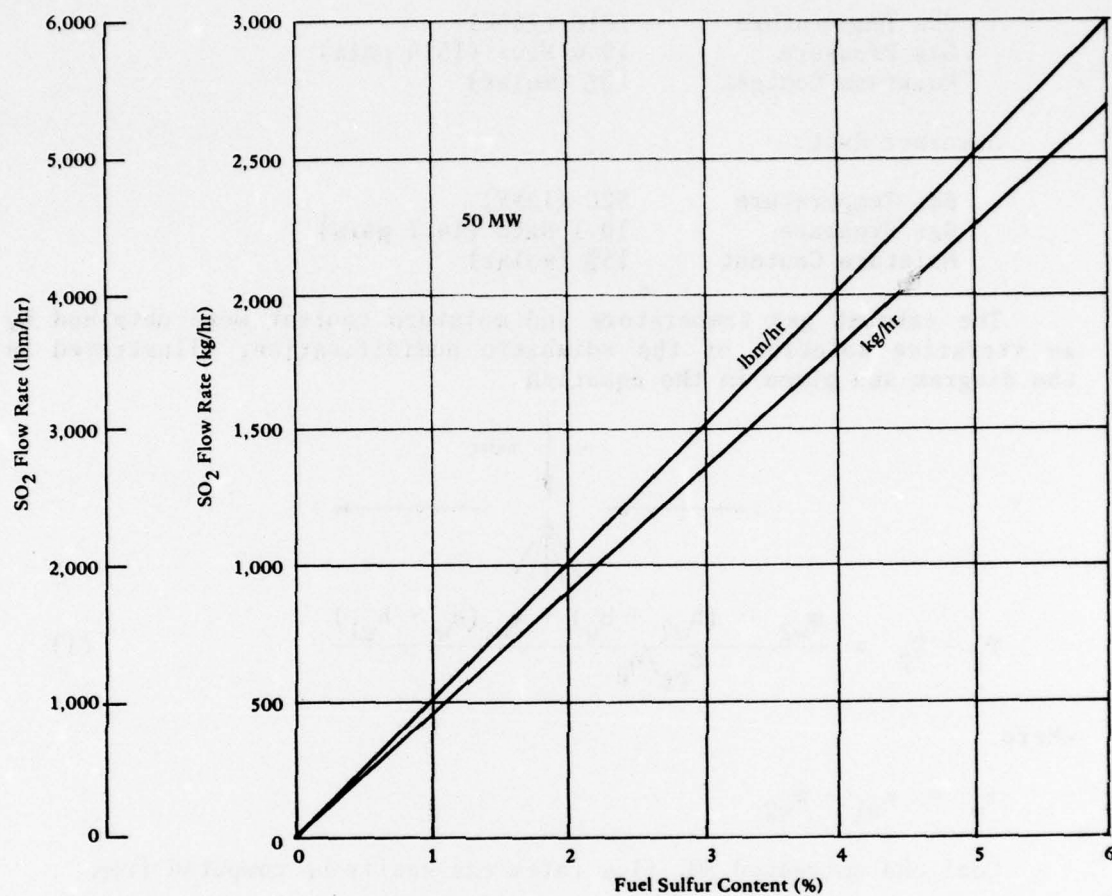


Figure 2. Untreated sulfur dioxide flow rate. (Multiply flows by 10 for 500 MW capacity.)

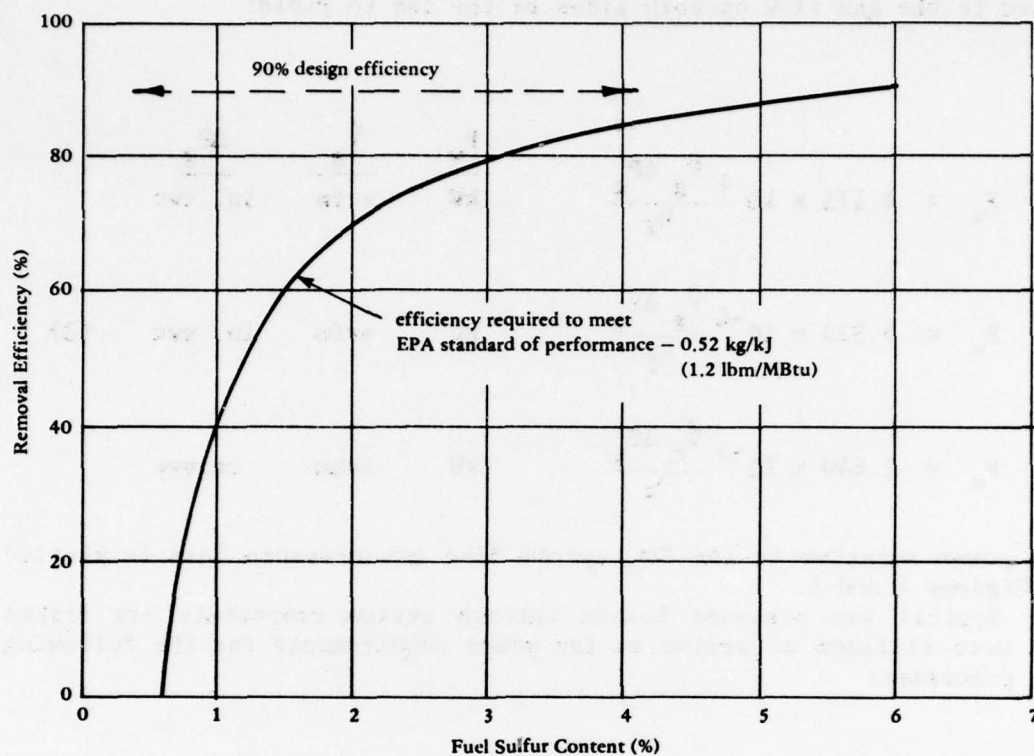


Figure 3. Design sulfur dioxide removal efficiency relative to EPA emission regulation for new units.

Fan and Pump Power Requirements

The fan power equation is derived from energy considerations applied to the gas flow on both sides of the fan to yield:

$$\begin{aligned}
 P_w &= 1.173 \times 10^{-4} \frac{\dot{V}_g \Delta P_g}{\eta_F} & \frac{P_w}{\text{kW}} & \quad \frac{\dot{V}_g}{\text{acfm}} & \quad \frac{\Delta P_g}{\text{in. vwc}} \\
 P_w &= 1.573 \times 10^{-4} \frac{\dot{V}_g \Delta P_g}{\eta_F} & \text{hp} & \quad \text{acfm} & \quad \text{in. vwc} \quad (3) \\
 P_w &= 1.640 \times 10^{-3} \frac{\dot{V}_g \Delta P_g}{\eta_F} & \text{kW} & \quad \text{acmm} & \quad \text{cm vwc}
 \end{aligned}$$

Fan power relative to the SO₂ system flue gas pressure loss is plotted in Figures 4 and 5.

Typical gas pressure losses through system components are listed and were utilized to arrive at fan power requirements for the following SO₂ processes:

<u>Components</u>	<u>cm vwc</u>	<u>in. vwc</u>
Venturi Prescrubber	13	5
Spray Tower	10	4
Fixed Bed Absorber	30	12
Mobile Bed Absorber	30	12
Activated Char Absorber	46	18
Mist Eliminator	3	1

A fan efficiency of 75% was used when applying Equation 3 to the candidate SO₂ systems.

A similar analysis leads to the pump power relationship for process liquor flows.

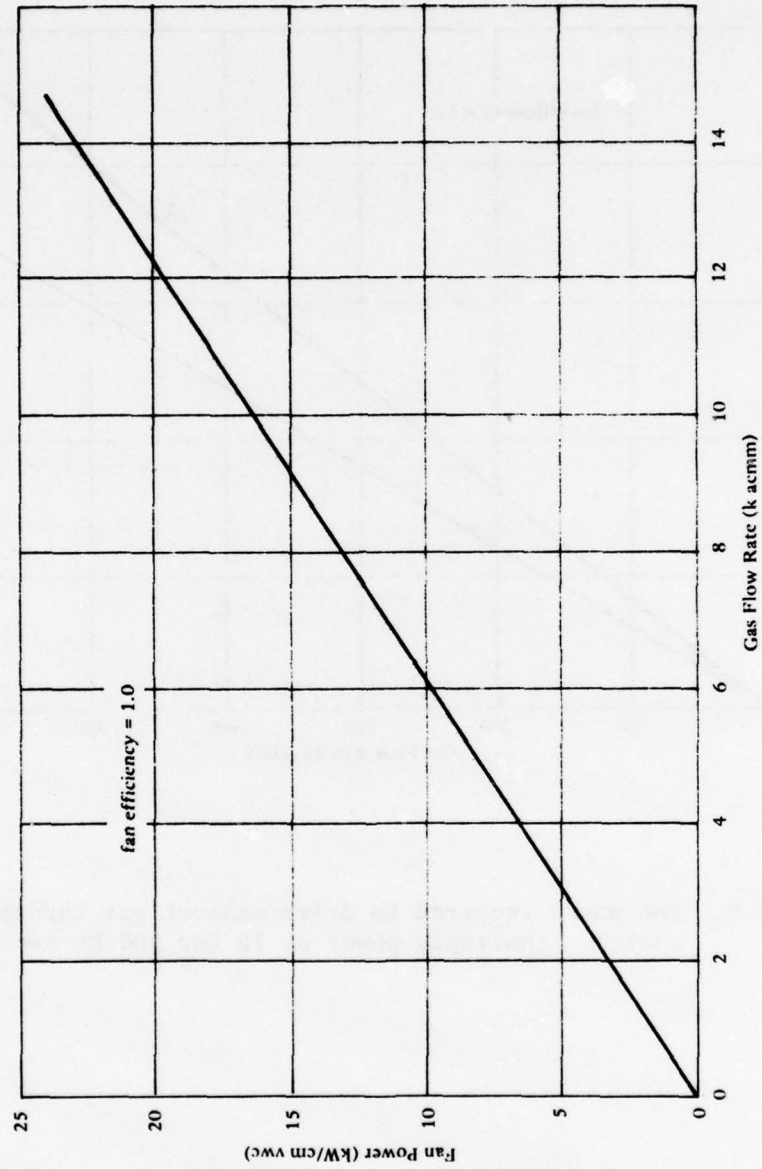


Figure 4. Fan power in metric units required to drive exhaust gas through SO₂ system. (Multiply power by 10 for 500 MW² capacity.)

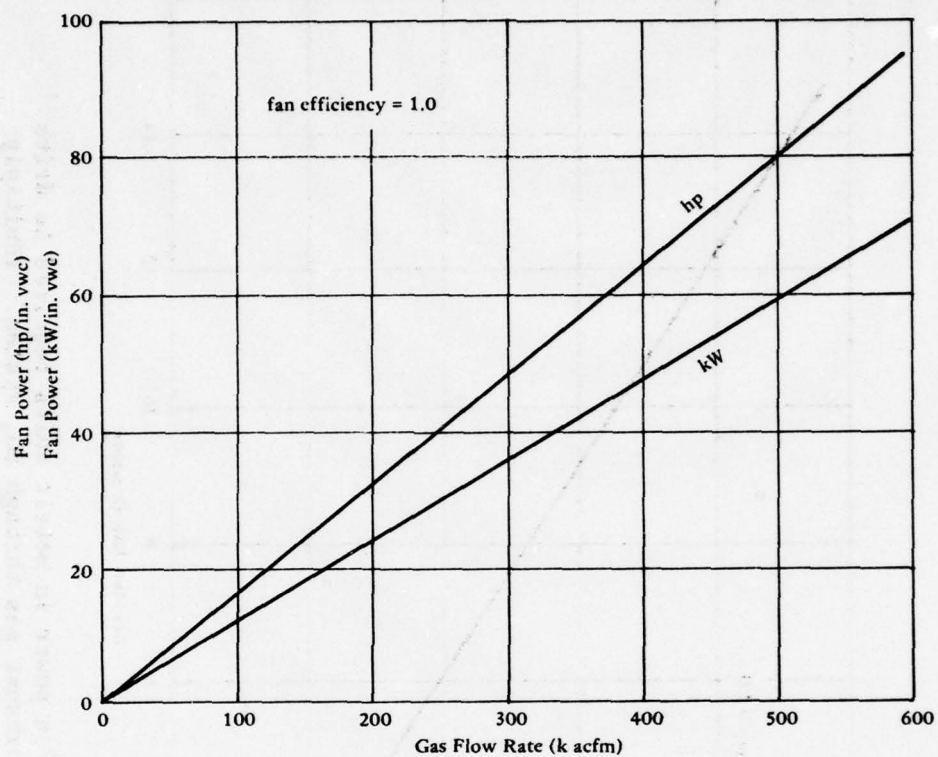


Figure 5. Fan power required to drive exhaust gas through SO_2 system. (Multiply power by 10 for 500 MW capacity.)

	$\frac{P_w}{\eta_p}$	$\frac{\dot{W}_L}{\eta_p}$	$\frac{\Delta P_L}{\eta_p}$	
$P_w = 4.35 \times 10^{-4} \frac{\dot{W}_L \Delta P_L}{\eta_p}$	kW	gpm	psi	
$P_w = 5.83 \times 10^{-4} \frac{\dot{W}_L \Delta P_L}{\eta_p}$	hp	gpm	psi	(4)
$P_w = 1.67 \times 10^{-4} \frac{\dot{W}_L \Delta P_L}{\eta_p}$	kW	lpm	nsc	

Parametric graphs of relative pump power requirements are shown in Figures 6 and 7 for convenient analyses. A pump efficiency of 60% is typical for slurry flows; 75% is more representative of clear liquor flows. These flows were adopted to arrive at pump power for the candidate processes analyzed.

The relationship for prediction of liquor flow pressure losses in piping systems is considerably more variable than the flue gas situation.

$$\Delta P_L = \rho_L H + f \frac{L}{d} \frac{\rho_L V_L^2}{2g_o} + K_A \frac{\rho_L V_L^2}{2g_o} + \Delta P_{sn} + \Delta P_{cv} \quad (5)$$

$$\Delta P_{cv} = \frac{F_M^2 - 1}{F_M^2} \Delta P_L \quad (6)$$

The control valve relationship is a function of the flow margin desired over nominal design conditions F_M . All terms but the pressure loss due to pumping to higher elevations ($\rho_L H$) are a function of dynamic pressure drop ($\rho_L V_L^2 / 2g_o$). Figure 8 contains the dynamic pressure drop variation with liquor velocity, and elevation pressure losses appear in Figure 9.

The following conditions were set for determining piping system pressure losses for each of the candidate processes:

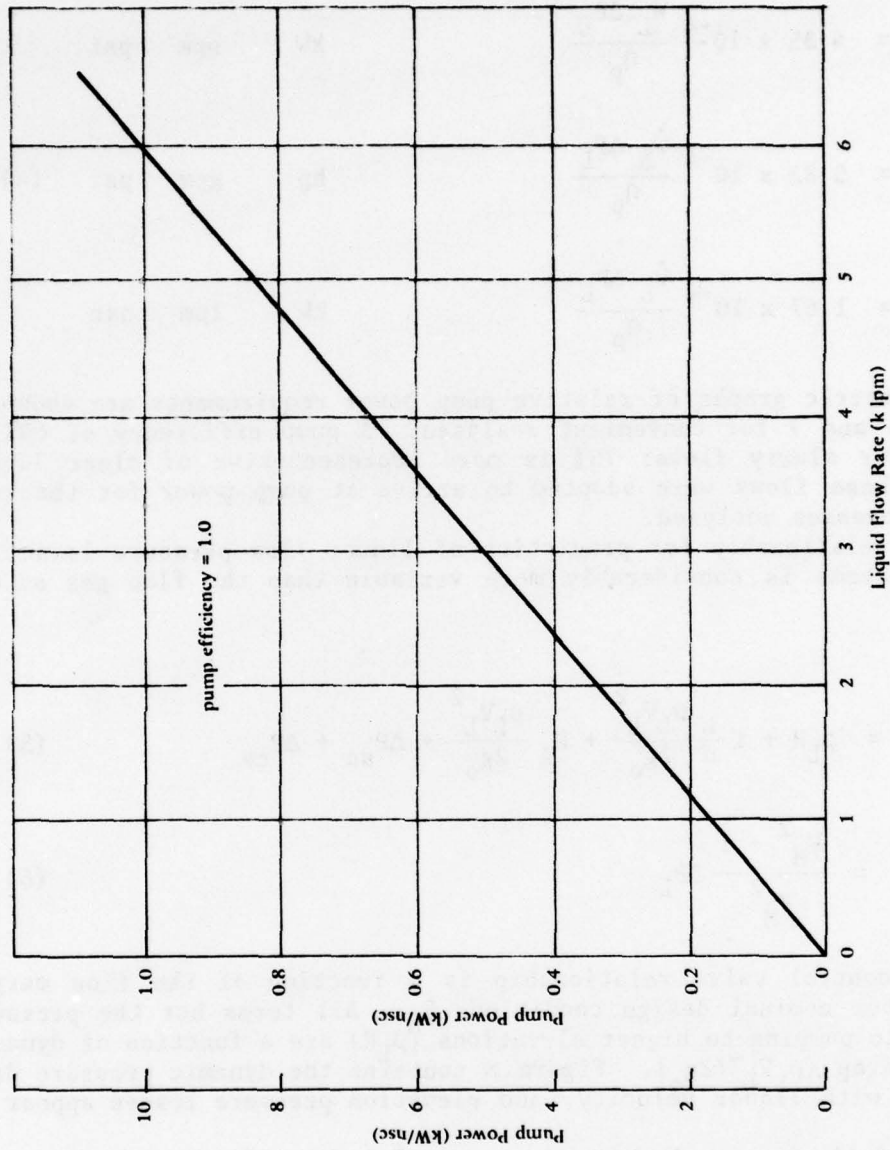


Figure 6. Liquid pump power requirements in metric units.
(Multiply power by 10 for 500 MW capacity.)

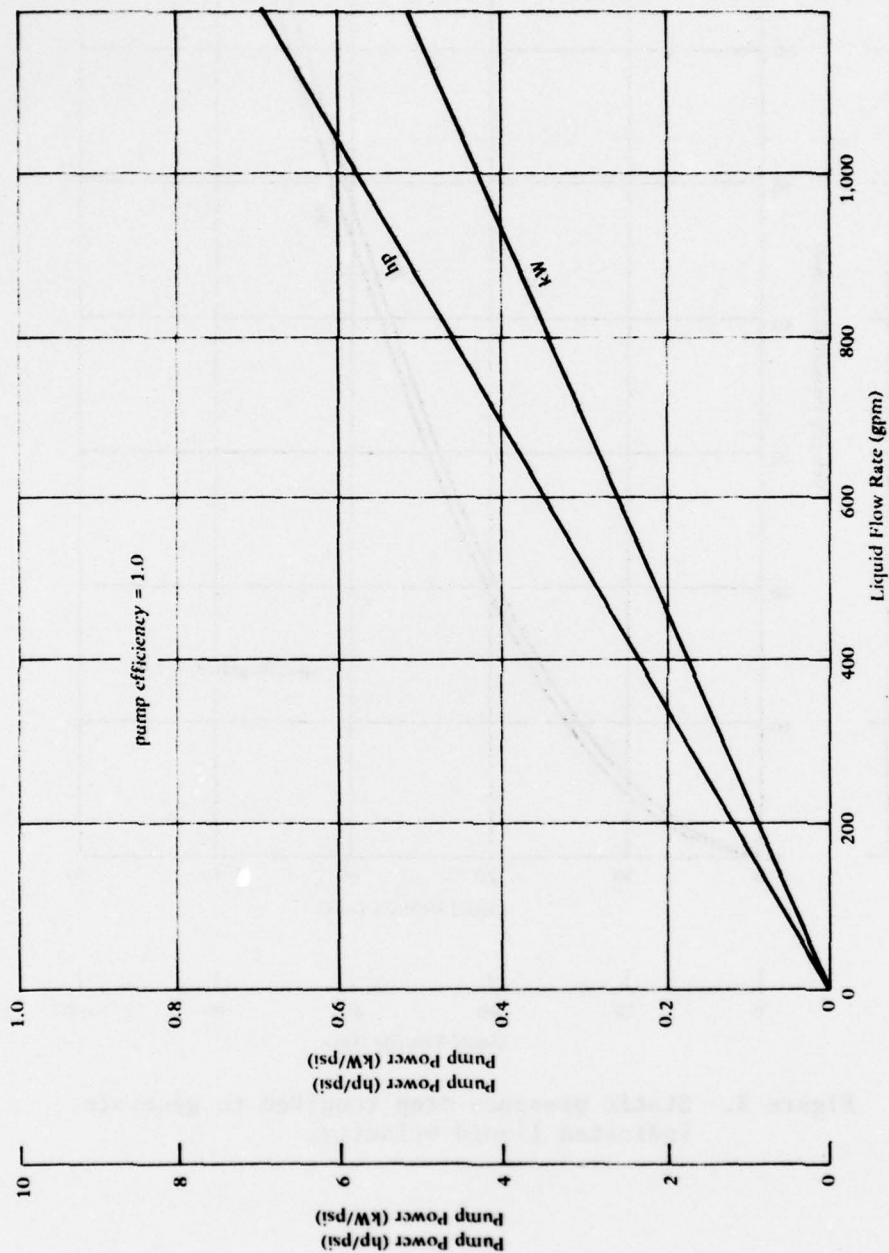


Figure 7. Liquid pump power requirements. (Multiply power by 10 for 500 MW capacity.)

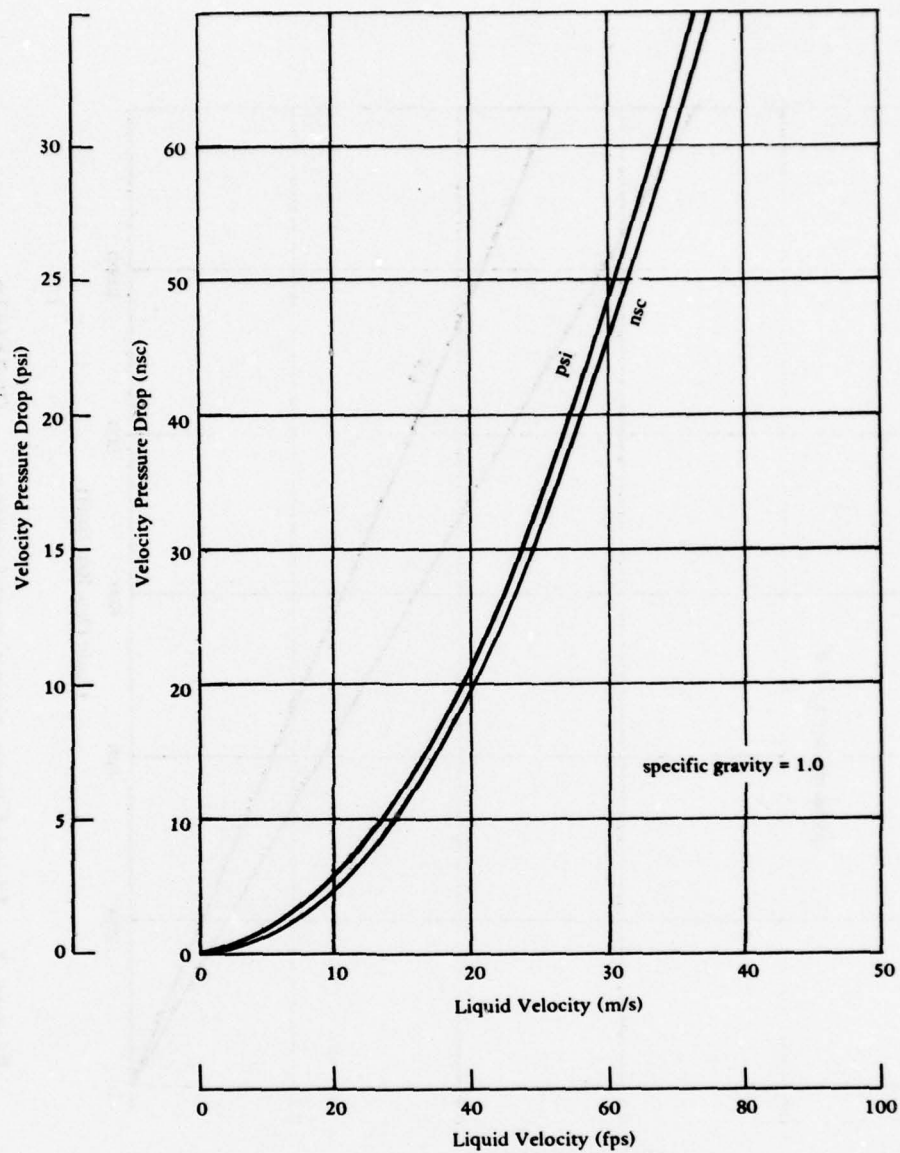


Figure 8. Static pressure drop required to generate indicated liquid velocity.

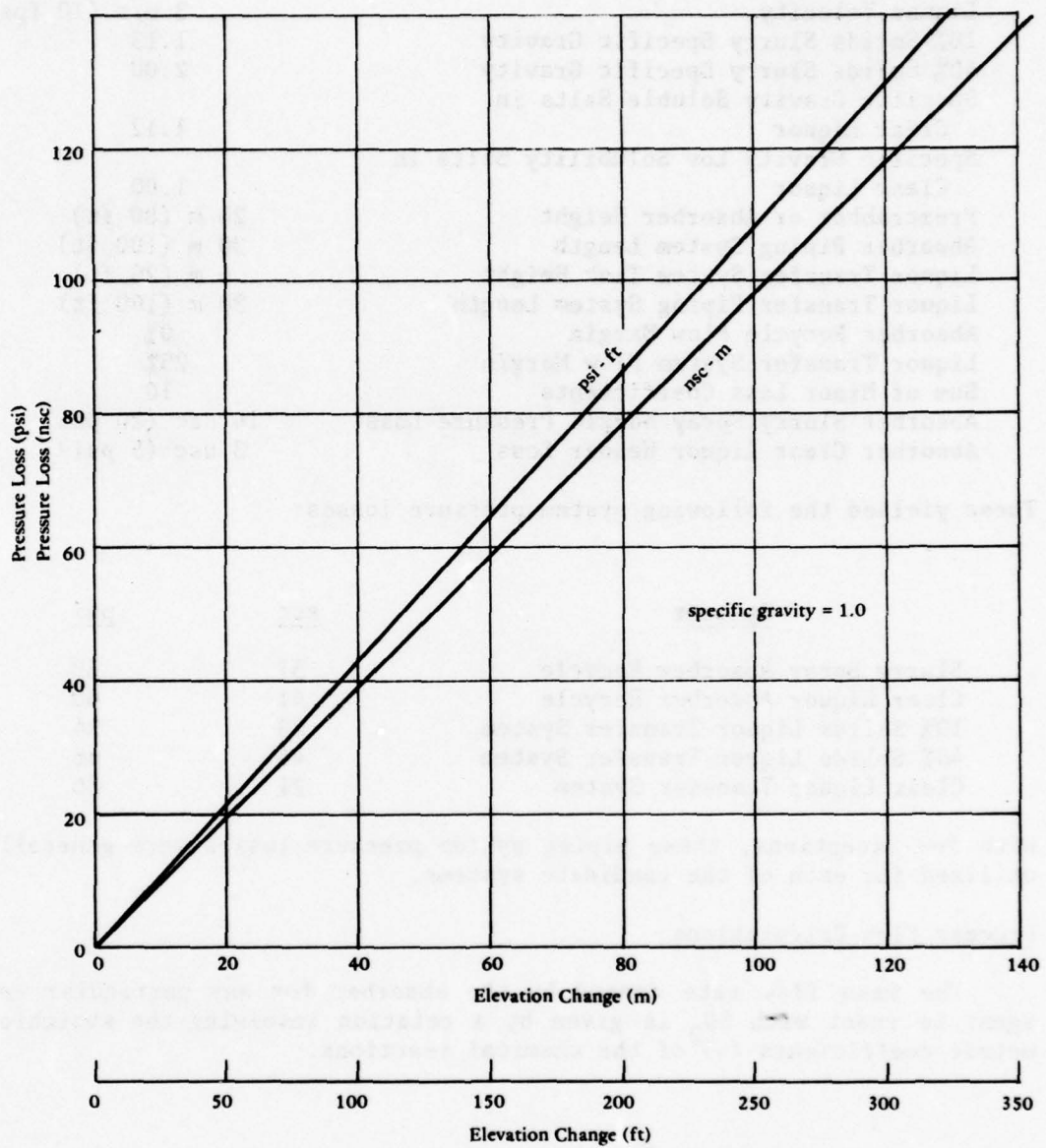


Figure 9. Pressure loss due to pumping liquor to higher elevations.

Conditions

Liquor Velocity	3 m/s (10 fps)
10% Solids Slurry Specific Gravity	1.13
40% Solids Slurry Specific Gravity	2.00
Specific Gravity Soluble Salts in Clear Liquor	1.12
Specific Gravity Low Solubility Salts in Clear Liquor	1.00
Prescrubber or Absorber Height	24 m (80 ft)
Absorber Piping System Length	30 m (100 ft)
Liquor Transfer System Tank Height	6 m (20 ft)
Liquor Transfer Piping System Length	30 m (100 ft)
Absorber Recycle Flow Margin	0%
Liquor Transfer System Flow Margin	25%
Sum of Minor Loss Coefficients	10
Absorber Slurry Spray Nozzle Pressure Loss	14 nsc (20 psi)
Absorber Clear Liquor Header Loss	3 nsc (5 psi)

These yielded the following system pressure losses:

<u>Systems</u>	<u>nsc</u>	<u>psi</u>
Slurry Spray Absorber Recycle	57	83
Clear Liquor Absorber Recycle	41	60
10% Solids Liquor Transfer System	23	34
40% Solids Liquor Transfer System	46	66
Clear Liquor Transfer System	21	30

With few exceptions, these piping system pressure losses were generally utilized for each of the candidate systems.

Process Flow Calculations

The mass flow rate demand by the absorber for any particular reagent to react with SO_2 is given by a relation involving the stoichiometric coefficients (ν)² of the chemical reactions.

$$\dot{W}_R = \sum_1^P \frac{\nu_R M_{wR}}{\nu_{\text{SO}_2} M_{w\text{SO}_2}} \frac{F_{RP} \dot{W}_{\text{SO}_2}}{F_{URP}} \quad (7)$$

Similarly, the mass flow of any one product generated in the absorber is available from the following relationship

$$\dot{W}_P = \sum_1^R \frac{v_P M_{WP}}{v_R M_{WR}} F_{RP} F_{URP} \dot{W}_R \quad (8)$$

where the reagent is consumed by the reaction with SO_2 in Equation 7.

Slurried liquor flow rates required for absorber bleed streams to remove product salts as they are generated in the recycle loop can be calculated from known product and reagent mass flows.

$$\dot{W}_L = \frac{\sum_1^P \dot{W}_P + \sum_1^R \sum_1^P (1 - F_{URP}) F_{RP} \dot{W}_R}{F_{SS} \rho_w}$$

Equation 9 was used to calculate all thickener underflows as well as absorber bleed and return slurries. In this analysis, thickener performance was fixed at 40% solids in the underflow, and vacuum filter cake was assumed to be 70% solids. A slightly modified version is used to calculate lime or limestone preparation slurries.

$$\dot{W}_L = \frac{\sum_1^R \dot{W}_R}{F_{SS} \rho_w \left(1 + \frac{1}{F_{SS} \rho_w} \sum_1^R S_R \right)} \quad (10)$$

If the product is completely dissolved, the liquor flow relationship takes on a different form.

$$\dot{W}_L = \frac{\dot{W}_P}{X_P F_{RG}} \quad (11)$$

The product requiring the greatest liquor flow rate is the controlling factor in setting the necessary liquor flow. Product concentrations were usually held near the solubility limit (S_R) to minimize liquor flow rates.

The listing or deriving of equations for crystalizer steam requirements, sand heater fuel flow, exhaust gas reheat fuel demand, condenser or char cooler water flow rates, or heated sand recirculation rates are omitted for brevity. These calculations are usually accomplished by a simple heat balance, and results are included in Table 1, along with all the other process flow rates. Space considerations have limited the number of process liquor flows to the major ones shown in Table 1, although all flows indicated on the process diagrams were determined and included in these analyses.

Table 1. System Operating Parameters at Full Load (500-MW and 1% sulfur fuel)

Item	Type of Units	Lime Slurry	Limestone Slurry	Dilute Acid	Dilute Double Alkali	Concentrated Double Alkali	Sodium Sulfite/Bisulfite	Activated Charcoal
Exhaust Gas Flow Rate	acmm acfm	38,953 1,376,430	38,953 1,376,430	38,953 1,376,430	38,953 1,376,430	38,953 1,376,430	38,953 1,376,430	43,257 1,528,500
SO ₂ Flow Rate	kg/min lb/min	76 167	76 167	76 167	76 167	76 167	76 167	76 167
Fan Power	kW hp	2,505 3,360	2,505 3,360	4,418 5,924	4,418 5,924	4,418 5,924	4,418 5,924	4,423 5,930
Pump Power	kW hp	5,028 6,742	5,028 6,742	2,215 2,966	2,252 3,016	2,093 2,802	2,766 3,704	66 88
Reheat/Sand Heater Oil	l/min gpm	35.6 9.4	35.6 9.4	35.6 9.4	35.6 9.4	35.6 9.4	35.6 9.4	11.4 3.0
Process Steam Flow	kg/min lb/min	— —	— —	— —	— —	— —	716 1,579	— —
Prescrubber Recycle Flow	l/min gpm	— —	— —	78,122 20,640	78,122 20,640	78,122 20,640	78,122 20,640	— —
Absorber Recycle Flow	l/min gpm	312,490 82,560	312,490 82,560	145,830 38,528	145,830 38,528	145,830 38,528	145,830 38,528	— —
Absorber Bleed Rate	l/min gpm	2,263 (10%S) 598 (10%S)	2,369 (10%S) 626 (10%S)	11,620 3,070	19,667 5,196	2,347 620	1,480 391	985 (kg/min) 2,171 (lb/min)
Reagent Flow	kg/min lb/min	89 196	158 348	121 266	68 149	74 163	0.5 1	96 211
		CaO	CaCO ₃	CaCO ₃	CaO	CaO	CaO	maximum char
(Natural Gas — scmm) (Natural Gas — scfm)	kg/min lb/min	19 42	19 42	20 45	20 45	20 45	40 1,425	40 1,425
		stabilizer	stabilizer	stabilizer	stabilizer	stabilizer	natural gas	natural gas
	kg/min lb/min	— —	— —	0.5 ~1	14 31	14 36	12 26	13 29
		— —	— —	Fe ₂ (SO ₄) ₃	Na ₂ CO ₃	Na ₂ CO ₃	Na ₂ CO ₃	minimum char

continued

Table 1. Continued

Item	Type of Units	Lime Slurry	Limestone Slurry	Dilute Acid	Dilute Double Alkali	Concentrated Double Alkali	Sodium Sulfite/Bisulfite	Activated Charcoal
Product Solids	kg/min	82	82	203	204	15	38	36
	lb/min	180*	180**	448	449	34	83	83
		CaSO ₄ 2H ₂ O	CaSO ₄ 2H ₂ O	CaSO ₄ 2H ₂ O	CaSO ₄ 2H ₂ O	CaSO ₄ 2H ₂ O	S	S
	kg/min	111	111	2	2	188	35	-
	lb/min	244	244	5	4	415	78	-
		CaSO ₃ 2H ₂ O	CaSO ₃ 2H ₂ O	CaCO ₃	Ca(OH) ₂	CaSO ₃ 2H ₂ O	Na salt cake	-

Note: 1. To adjust all flows to new plant capacities, multiply by new MW/500.

2. To adjust all flows to new fuel sulfur contents, multiply by new fuel S%/1% (exception—exhaust gas flow is not a function of sulfur content).

*Plus 65 lb Unreacted Ca(OH)₂

**Plus 87 lb Unreacted CaCO₃

Energy and Reagent Unit Costs

<u>Units</u>	<u>Costs</u>
Electrical Power	20 mills/kWh
Delivered Coal	\$0.49/GJ (\$0.52/MBtu)
Natural Gas	\$1.61/GJ (\$1.70/MBtu)
Steam Cost	\$2.15/GJ (\$2.27/MBtu)
Distillate Fuel Oil	\$2.63/GJ (\$2.77/MBtu)
90% Lime Delivered	\$51/M ton (\$46/ton)
85% Limestone Delivered	\$34/M ton (\$31/ton)
Filter Cake Stabilizer	\$56/M ton (\$51/ton)
Soda Ash Delivered	\$80/M ton (\$73/ton)
Fe(OH) ₃ Delivered	\$133/M ton (\$121/ton)
Activated Char	\$286/M ton (\$260/ton)
Disposal Cost	\$0.66/M ton (\$0.60/ton)
Sulfur Credit	\$24/M ton (\$22/ton)
Capital Cost SO ₂ System	\$150/kW
Capital Cost of ² Steam	
Electric Unit	\$350/kW
Sodium Salt Cake Credit	\$11/M ton (\$10/ton)
Maintenance Costs	2% Capital Investment/Yr
Operating Labor Cost	\$15/hr

Economics

The basic operating cost relationships are quite simple to derive and easy to use.

$$C_o = U \dot{W} t L_c \quad \$/\text{yr} \quad (12)$$

$$C_o = \frac{U \dot{W} (10^3)}{G} \quad \text{mills/kWh} \quad (13)$$

$$C_o = \frac{10^6 U \dot{W}}{\text{HR}_N G} \quad \$/\text{MBtu} \quad (14)$$

Process economics are tabulated in Table 2 for each candidate SO₂ removal system.

Table 2. System Operating Costs at Full Load (1% sulfur fuel)

Cost Items	Type of Units	Lime Slurry	Limestone Slurry	Dilute Acid	Dilute Double Alkali	Concentrated Double Alkali	Sodium Sulfite/Bisulfite	Activated Charcoal
Fan Power Cost	mills/kWh	0.1002	0.1002	0.1770	0.1770	0.1770	0.1770	0.1768
Pump Power Cost	mills/kWh	0.2000	0.2000	0.0890	0.0901	0.0837	0.1100	0.0026
Reheat Fuel Oil	mills/kWh	0.4319	0.4319	0.4319	0.4319	0.4319	0.4319	—
Sand Heater Fuel Oil	mills/kWh	—	—	—	—	—	—	0.1370
Process Steam Cost	mills/kWh	—	—	—	—	—	0.397	—
Reagent Cost	mills/kWh	0.6010 CaO	0.7490 CaCO ₃	0.5730 CaCO ₃	0.4570 CaO	0.5000 CaO	0.0030 CaO	3.290* maximum char
	mills/kWh	0.1290 stabilizer	0.1290 stabilizer	0.1380 stabilizer	0.1380 stabilizer	0.1380 stabilizer	0.2975 natural gas	0.2910 natural gas
	mills/kWh	—	—	0.0035 Fe ₂ (OH) ₃	0.1350 Na ₂ CO ₃	0.1580 Na ₂ CO ₃	0.1140 Na ₂ CO ₃	0.4520 minimum char
Disposal Costs (credits)	mills/kWh	0.0306 filter cake	0.0312 filter cake	0.0283 filter cake	0.0298 filter cake	0.0301 filter cake	(0.1100) S	(0.1100) S
	mills/kWh	—	—	—	—	—	(0.0500) salt cake	0.0076 waste char
Operating Labor Cost	mills/kWh	0.1160	0.1160	0.1160	0.1160	0.1160	0.1160	0.1160
Maintenance Cost	mills/kWh	0.4200	0.4200	0.4200	0.4200	0.4200	0.4200	0.4200
Total Costs	mills/kWh	2.0287	2.1773	1.9767	1.9948	2.0547	1.9064	4.3310* -1.4930
	10 ⁶ \$/yr	7.1086	7.6293	6.9264	6.9898	7.1997	6.6800	15.1760* -5.2315

Note: 1. To adjust all costs to new fuel sulfur content, multiply by new fuel S%/1% (except fan power costs are not a function of fuel sulfur content).

2. Total costs in 10⁶ \$/yr corresponds to a 500-MW unit capacity.

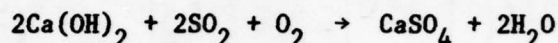
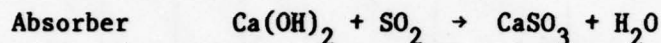
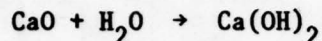
3. To convert costs from mills/kWh to \$/MBtu, multiply by 0.10.

*Maximum char loss values.

SYSTEMS STUDIED

Lime Slurry System

The chemistry of lime slurry scrubbing is straight forward with CaSO_4 and CaSO_3 produced in the absorber on reacting with SO_2 . The lime forms Ca(OH)_2 when contacted with water.



Approximately 40% of the SO_2 reacts to form CaSO_4 and 60% forms CaSO_3 (3). A great deal of variability in lime utilization (F_{URP}) in slurry systems is reported in the literature, ranging from 50% to 100%. The fact that slurry scrubbing relies on suspended lime particles as the reacting media renders high utilization values doubtful. A lime utilization of 75% was selected for this comparison.

The process diagram in Figure 10 shows a closed loop operation, which conserves water and reduces the size of the disposal pond. Extensive scale buildup in the absorber internals and sump area has plagued the lime slurry systems over the history of their operation, particularly during closed loop operation. A precipitator ahead of the absorber is recommended to reduce the solids level in the absorber slurry, and an open spray tower absorber design is a necessity to prevent plugging of the gas flow and liquor flow paths. Basically, scale buildup will always be a problem with slurry systems, since the return liquor to the absorber is saturated in CaSO_3 and CaSO_4 and becomes supersaturated in the absorber when the Ca(OH)_2 is converted to CaSO_3 or CaSO_4 .

The system advantage is that operation is relatively simple due to the small number of components.

System disadvantages include:

1. Scale buildup causes high maintenance even with an open spray tower absorber.
2. Mist eliminator scaling and plugging are continuous maintenance items.
3. Particulate emission performance is well below that of clear liquor processes, due to entrained solids.
4. Large quantities of lime and gypsum movement in and out of the plant area conflict with power plant operation.
5. Water pollution is a problem of the CaSO_3 product, as are CaSO_3 crystal growth difficulties in the thickener.

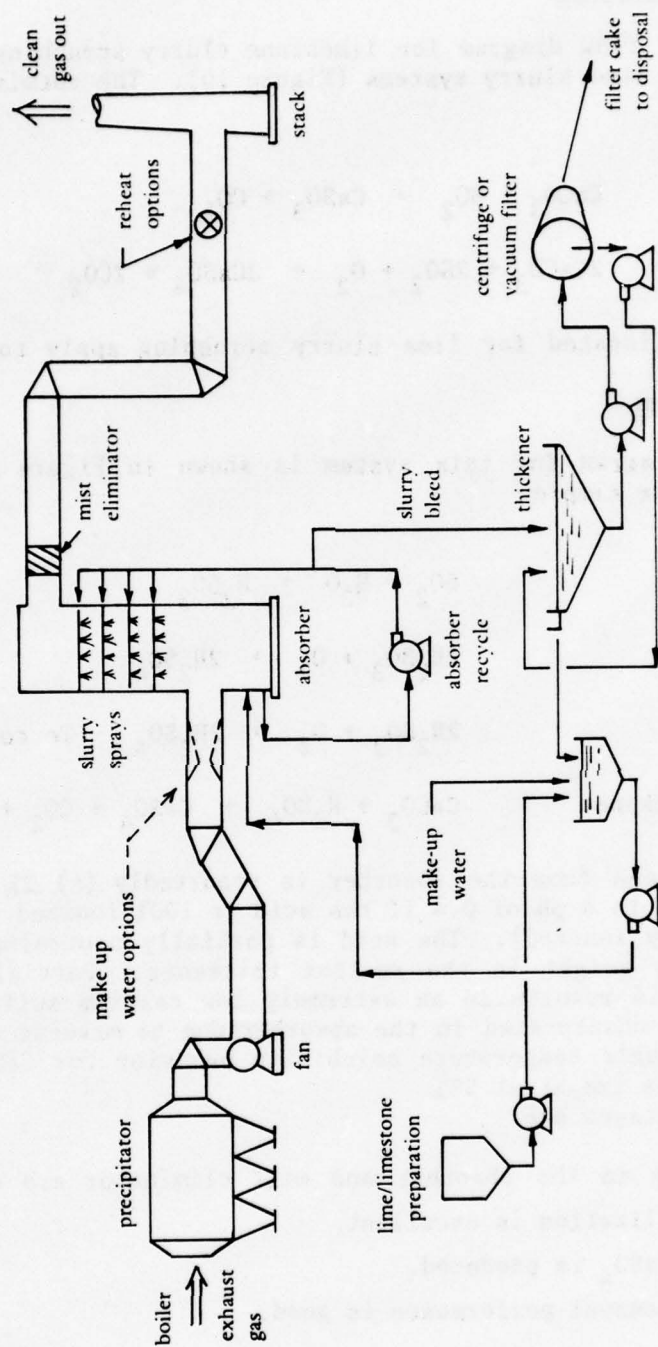
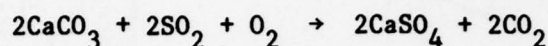
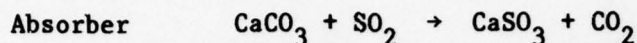


Figure 10. Lime or limestone slurry SO_2 removal system.

Limestone Slurry System

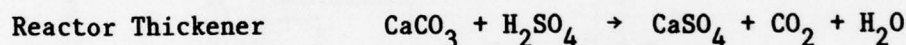
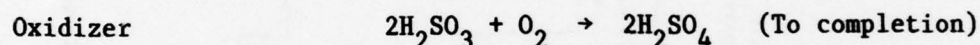
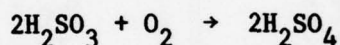
The process flow diagram for limestone slurry scrubbing is identical to that for lime slurry systems (Figure 10). The chemistry is also similar.



The comments delineated for lime slurry scrubbing apply to limestone.

Dilute Acid System

The flow diagram for this system is shown in Figure 11, and the chemistry is quite simple.



The acid bleed from the absorber is reportedly (4) 2% by weight, which corresponds to a pH of 0.4 if the acid is 100% ionized (or about 1 to 2 if partially ionized). The acid is partially neutralized to a 1% acid solution by weight in the reactor thickener. Partial neutralization of the acid results in an extremely low calcium sulfate concentration, that is unsaturated in the absorber due to make-up water addition and a favorable temperature solubility behavior for CaSO_4 . Limestone utilizations are about 98%.

System advantages are:

1. Scale buildup in the absorber and mist eliminator are eliminated.
2. Limestone utilization is excellent.
3. Almost pure CaSO_4 is produced.
4. Particulate removal performance is good.

System disadvantages include:

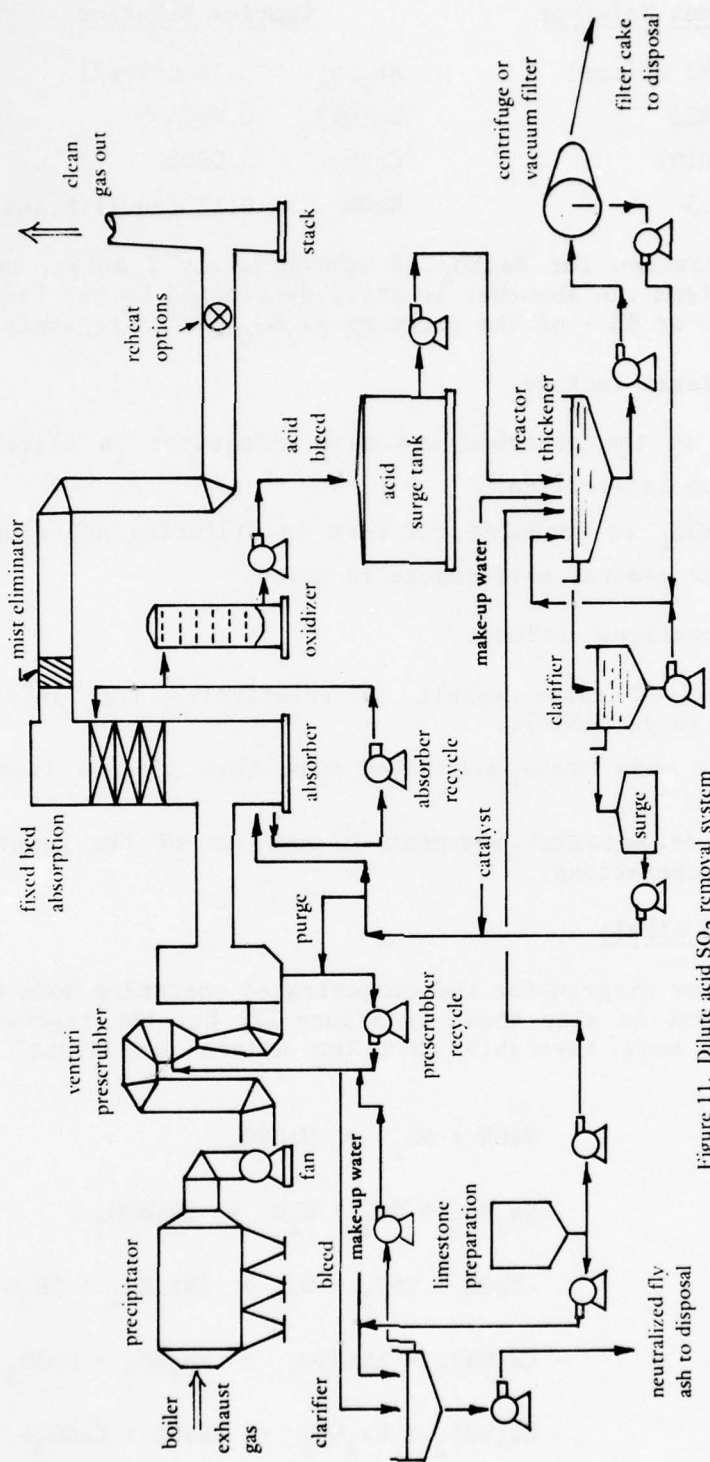


Figure 11. Dilute acid SO_2 removal system

Figure 11. Dilute acid SO_2 removal system.

Single Component Solution

Na_2SO_4	1.37 moles/l
$\text{Ca}(\text{OH})_2$	0.022
CaSO_4	0.0151
NaOH	27.3

Complex Solution

Na_2SO_4	1.16 moles/l
$\text{Ca}(\text{OH})_2$	0.0005
CaSO_4	0.0002
NaOH	0.12 (equilibrium)

The design concentration for Na_2SO_4 is appropriately 1 molar, but the liquor bleed rate from the absorber is still determined by the fact that only 0.06 moles/l - or 6% - of the incoming Na_2SO_4 can be regenerated in the reaction tank.

Process advantages include:

1. Scale buildup in the absorber and mist eliminator is eliminated.
2. Lime utilization is excellent.
3. Almost pure CaSO_4 is produced for ease in filtering and disposal.
4. Good particulate removal performance is noted.

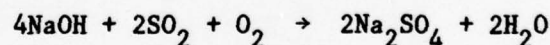
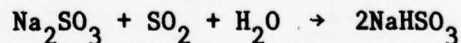
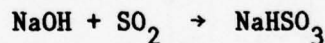
Process disadvantages include:

1. Large liquor bleed rates result in relatively large thickener, clarifier, and surge vessels.
2. Slightly higher pump costs are noted with this process than with some processes.
3. Large amounts of material movement in and out of the plant area interfere with operations.

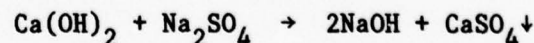
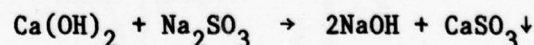
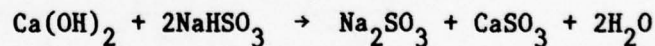
Concentrated Double Alkali

The process flow diagram for the concentrated operating mode of the double alkali process is also shown in Figure 12, but the regeneration chemistry is much more favorable than the dilute operational mode.

Absorber



Reaction Tank



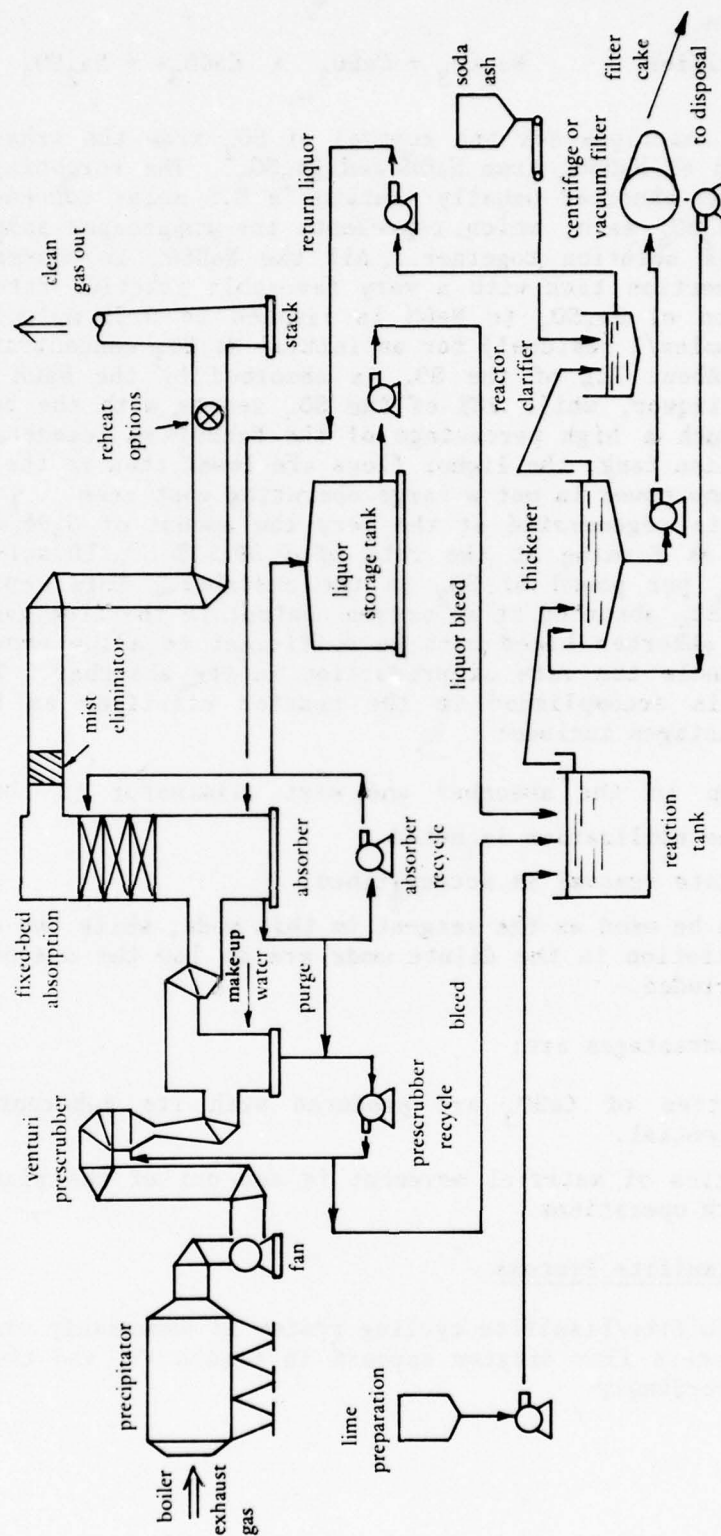


Figure 12. Double alkali SO₂ removal system, dilute and concentrated modes.

Reactor Clarifier



The primary reactions for the removal of SO_2 from the exhaust gas are the formation of NaHSO_3 from NaOH and Na_2SO_3 . The scrubbing solution bled from the absorber usually contains a 0.5 molar concentration of NaHSO_3 and Na_2SO_4 each, which represents the suppressed solubility limits of both in solution together. All the NaHSO_3 is converted to Na_2SO_3 in the reaction tank with a very favorable reaction rate. The further conversion of Na_2SO_3 to NaOH is limited to 0.36 moles/l converted (or 0.14 moles/l residual) for an initial Na_2SO_3 concentration of 0.5 molar (5). About 72% of the SO_2 is absorbed by the NaOH in the absorber return liquor, while 28% of the SO_2 reacts with the residual Na_2SO_3 . Since such a high percentage of the NaHSO_3 is regenerated to NaOH in the reaction tank, the liquor flows are lower than in the dilute mode, although pump power is not a large operating cost item.

The Na_2SO_4 is regenerated at the very low amount of 0.06 moles/l and is observed as forming at the rate of 0.00153% $\text{SO}_2/10^3\text{scf-\%O}_2$ in pounds of Na_2SO_4 per pound of SO_2 in the absorber. This represents about 8% of the SO_2 absorbed at an oxygen content in the flue gas of 4% by volume. The absorber bleed must be sufficient to allow enough regeneration to handle the rate of production in the absorber. The removal of CaSO_3 is accomplished in the reactor clarifier as before.

Process advantages include:

1. Scale buildup in the absorber and mist eliminator is obviated.
2. Excellent lime utilization is noted.
3. Good particulate removal is accomplished.
4. Limestone can be used as the reagent in this mode, while the equilibrium concentration in the dilute mode are so low the use of limestone is precluded.

Process disadvantages are:

1. Large quantities of CaSO_3 are produced with its inherent water pollution potential.
2. Large quantities of material movement in and out of the plant area interfere with operations.

Sodium Sulfite/Bisulfite Process

The sodium sulfite/bisulfite cycling system is remarkably simple in concept. The process flow diagram appears in Figure 13, and the chemistry follows accordingly.

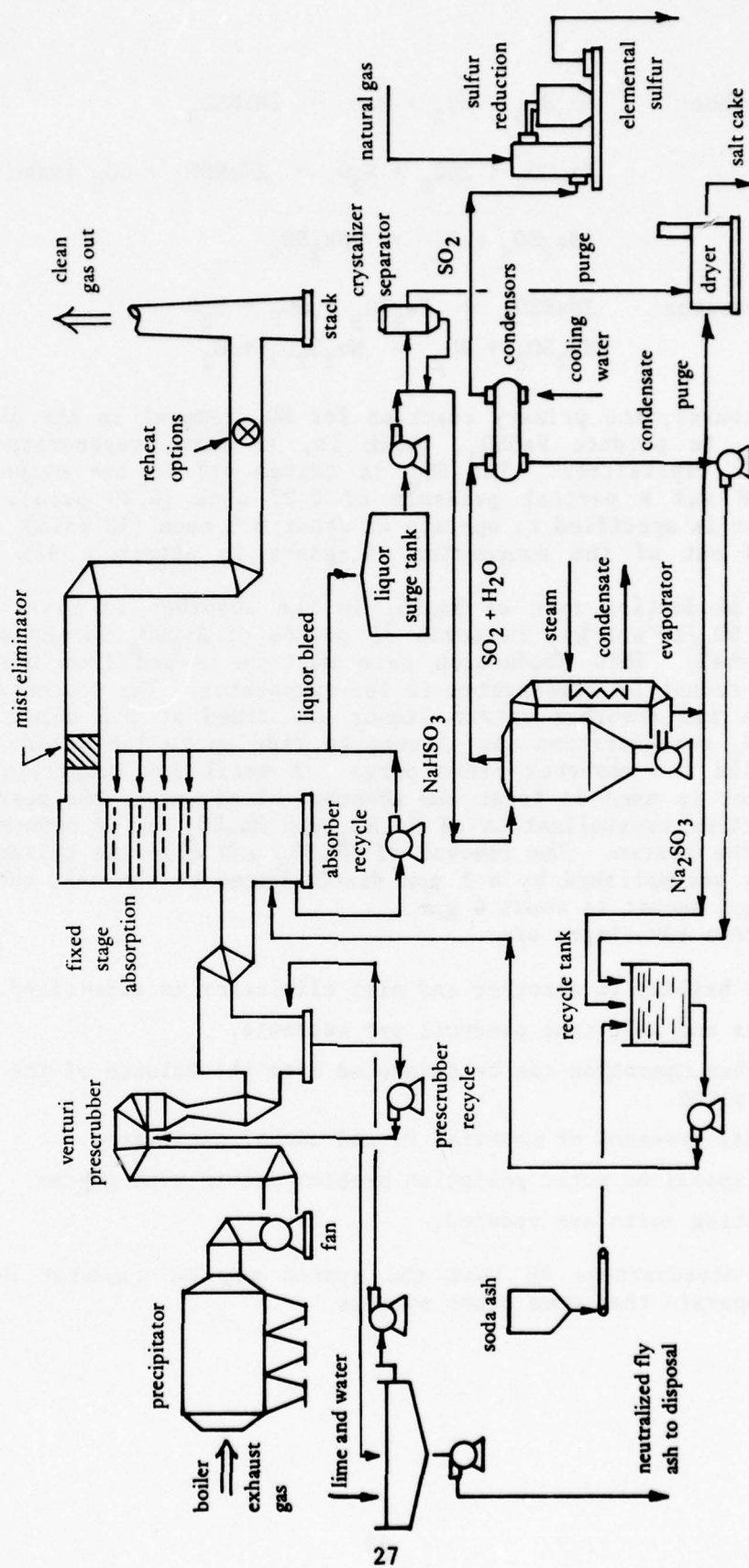
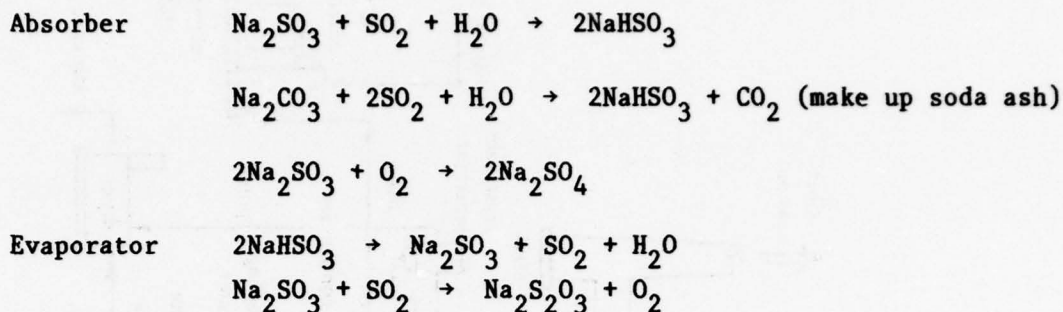


Figure 13. Sodium sulfite/bisulfite SO_2 removal system.



Of course, the primary reaction for SO_2 removal is the absorption by Na_2SO_3 to produce NaHSO_3 , which is, in turn, regenerated in the evaporator crystalizer. The SO_2 is driven off in the evaporator at some 210F and a partial pressure of 0.27 nsca (0.39 psia), and the evaporator is specified to operate at about 8.3 nsca (12 psia). Water is condensed out of the evaporator off-gases to attain a 92% rich SO_2 stream.

The production rate of Na_2SO_4 in the absorber is again equal to 0.00153% $\text{SO}_2/10^5 \text{ scf-}\% \text{O}_2$ in terms of pounds of Na_2SO_4 formed per pound SO_2 absorbed. This production rate must be purged from the system, since it cannot be regenerated in the evaporator. The concentration of Na_2SO_3 in the absorber return liquor was fixed at 0.8 moles/l, while the Na_2SO_4 concentration was allowed to ride up to 1.0 mole/l in order to minimize the absorber bleed purge. A small low temperature (40F) crystalizer is used to treat the absorber bleed purge, the result being the selective crystallization of Na_2SO_3 and Na_2SO_4 and a reduced sodium loss to the system. The removal of Na_2SO_3 and chloride buildup in the system is accomplished by a 1 gpm direct purge to the salt cake dryer. Both purges amount to about 4 gpm.

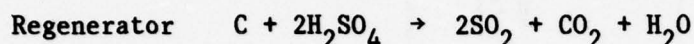
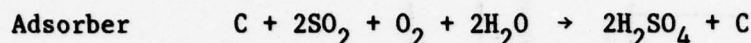
Process advantages are:

1. Scale buildup in absorber and mist eliminator is eliminated.
2. Sulfur and salt cake products are saleable.
3. Absorber operation can be decoupled from the balance of the SO_2 system.
4. Minimal movement of material in and out of plant area.
5. No disposal or water pollution problem exists with gypsum.
6. Operating costs are reduced.

The disadvantage is that the system may be somewhat more complex to operate than some other systems.

Activated Char Adsorption System

The process flow diagram for this system is available in Figure 14, and the chemistry for the adsorption of SO_2 by activated char is as follows:



The SO_2 is adsorbed as H_2SO_4 in the porous cavities of the char, which chemically reacts with the carbon in the char on being heated to 649°C ($1,200^\circ\text{F}$) during regeneration in the sand heater. This inevitably leads to an enlargement of the char pores and a corresponding reduction in physical strength. A stream 50% (by volume) rich in SO_2 is off-gassed in the regenerator for ultimate reduction to elemental sulfur in the sulfur reduction plant. After regeneration, the char is water-cooled to 200°F for re-entry into the absorber.

Operating experience with sulfur reduction by coal at the pilot plant level has not been successful to date (6), so operating costs for a conventional Claus plant were applied to this system for comparison. The char circulation rate around the system has been observed to range from 4 to 7 kg-char/kg- SO_2 (8-16 lb-char/lb- SO_2), with the more representative rate being 6 kg-char/kg- SO_2 (13 lb-char/lb- SO_2) as plotted (6). Since the activated char system has not been operated with all components simultaneously for a long enough period to establish char attrition rates, estimates were made to bound the area of probable consumption. The chemical losses are easily calculated to be 7 kg/min (16 lb/min) for the regenerator chemical reaction. Char abrasion losses are estimated from operating experience with thermal catalytic crackers (7) where alumina balls are lost at a rate of 0.6% of the circulation rate. This defines the lower limit of char abrasion loss. Unfortunately, char is not as strong as alumina where a tensile strength ratio of 15, alumina to char, is easily shown. If char loss due to abrasion is linear with tensile strength, the char attrition could be 9% of the circulation. This higher char loss estimate is believed to be conservative since the estimate makes no attempt to consider the further weakening caused by increased porosity due to regeneration cycles.

The activated char system is also reported to have the capability of removing NO from the exhaust gas, which is also an oxidation-reduction reaction with an additional chemical loss to the system.

System advantages are:

1. Saleable sulfur product.
2. Somewhat smaller amount of material movement in and out of the plant area.

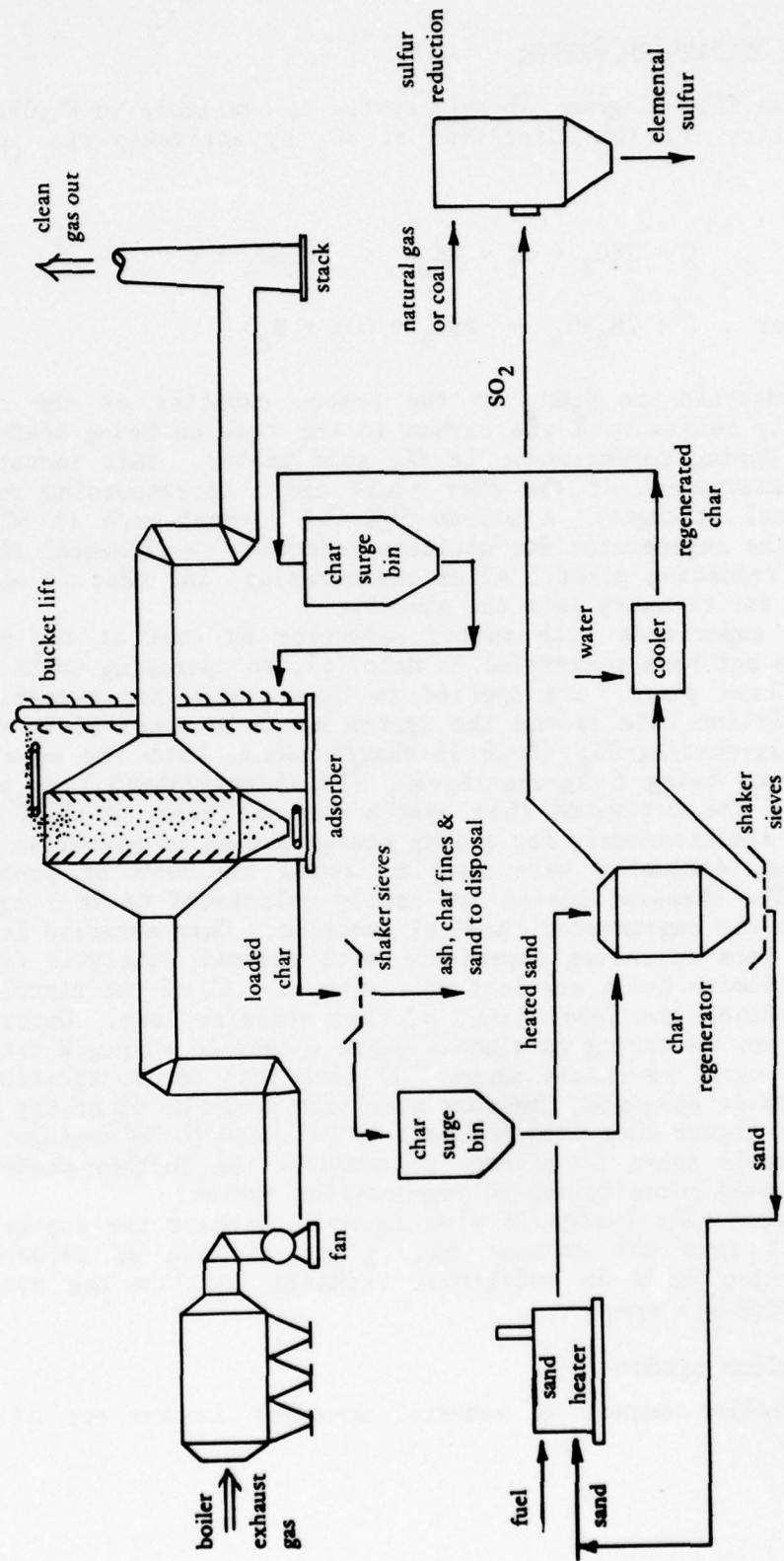


Figure 14. Activated char SO₂ removal system.

3. Requirement for stack gas reheat eliminated.

System disadvantages include:

1. Extreme risk in operating costs without conclusive char attrition experience.
2. Low reliability and high maintenance of solids handling equipment.
3. Potential safety hazards in handling hot char ranging from 93C to 649C (200F to 1,200F).

SUMMARY

The process operating parameters of each candidate can be compared in Table 1. Both dilute acid and dilute double alkali have high absorber bleed rates, which will be manifested in larger process vessels and relatively high capital cost, but will have the more attractive filter cake product (CaSO_4 rather than CaSO_3). All processes except the sodium sulfite/bisulfite and activated char systems involve large quantities of material movement in and out of the plant area, both in the form of lime or limestone (209 tons/day) and calcium salt products (300 tons/day). The only process utilizing significant quantities of process steam is the sodium sulfite/bisulfite system. The only processes with an attractive marketable product are the sodium sulfite and activated char processes.

Operating costs are tabulated in Table 2 and plotted as a function of fuel sulfur content in Figure 15. Operating costs for four of the processes are bunched together in the narrow band shown in Figure 15, to the extent that they are undistinguishable in cost. Limestone is somewhat higher and the sodium sulfite/bisulfite process is somewhat lower. The sodium sulfite systems could be reduced an additional 0.25 mills/kWh at 1% sulfur in the fuel if the evaporator were to be sized to run at off-peak electrical demand periods (which makes it look even more attractive). The extremely high risk in the activated char system is indicated by the estimated range in operating costs because of uncertainty in char attrition. Operating costs can be converted from mills/kWh to \$/MBtu by simply multiplying the numbers in Table 2 by 0.1.

The governing laws for scaling process flows and power consumption are embodied in Equations 1 through 14. Careful examination and the combining of these relationships demonstrate that all flows and pump power scale linearly with fuel sulfur content and steam generator capacity. Fan power, on the other hand, is only a function of unit capacity. Operating costs follow similar rules. This analysis forms the basis for the scaling laws outlined in Tables 1 and 2.

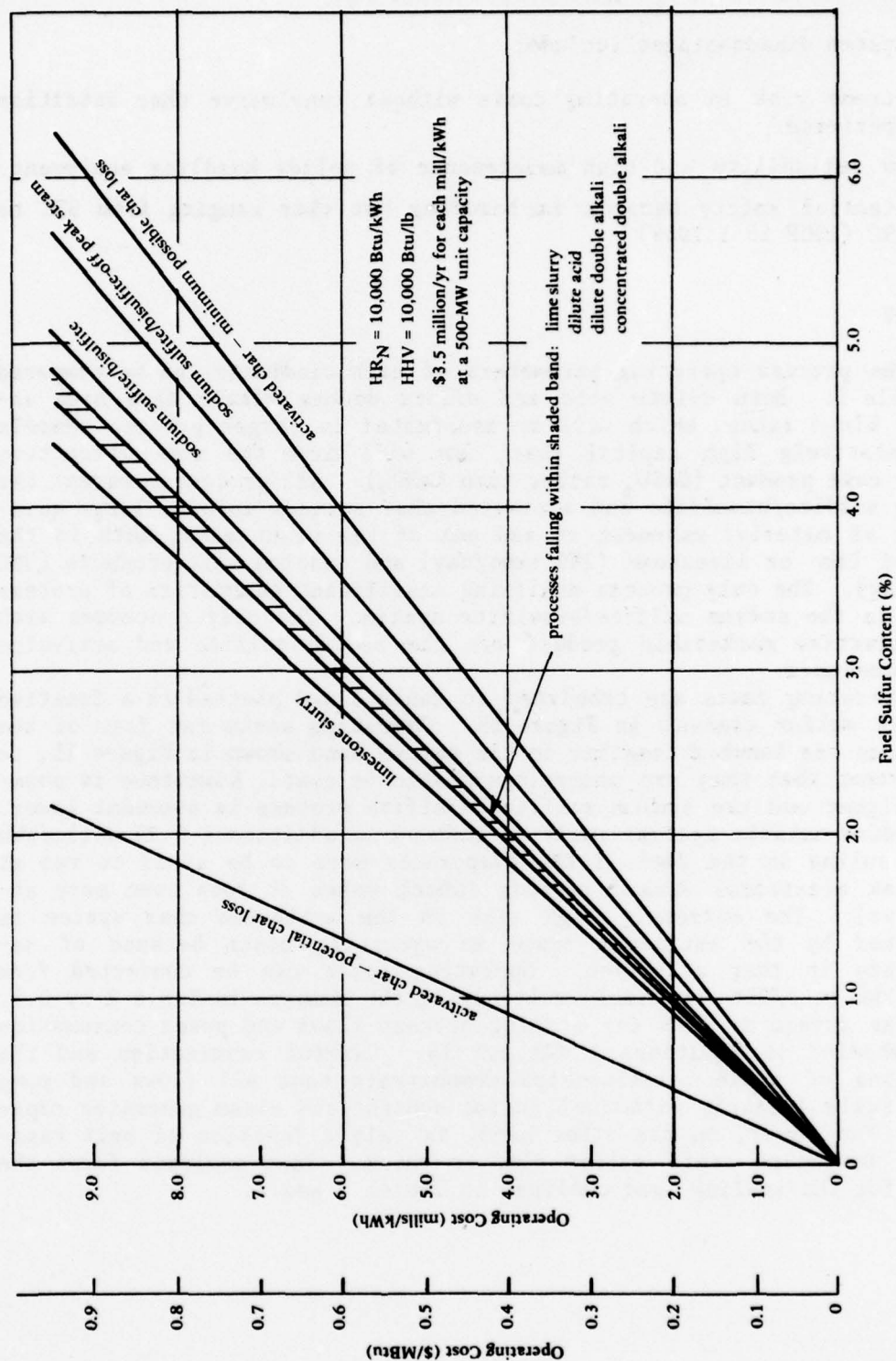


Figure 15. Comparative operating costs for candidate SO_2 removal systems.

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ACKNOWLEDGMENT

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NOMENCLATURE

C_o	Operating Cost (\$/yr; mills/kWh)
C_{pg}	Exhaust Gas Specific Heat (Cal/g-°C; Btu/lb-°F)
d	Inside Pipe Diameter (m; ft)
F_M	Liquor Flow Rate Margin Over Nominal Design
F_{RG}	Fraction of Absorber Product Regenerated
F_{RP}	Fraction of Reagent R Forming Product P
F_S	Fuel Sulfur Content
F_{SS}	Fraction of Suspended Solids in Slurry
F_{URP}	Utilization of Reagent R Forming Product P
f	Pipe Friction Factor
G	Steam-Electric Unit Generation Capacity (kW)
g_o	Gravitational Constant (M/s ² ; ft/s ²)
H	Absorber or Vessel Overall Height (m; ft)
HHV	Fuel Higher Heating Value (kJ/kg; Btu/lb)
HR_N	Steam-Electric Unit Net Heat Rate (kJ/kWh; Btu/kWh)
h_w	Make-Up Water Enthalpy (kJ/kg; Btu/lb-dry gas)
h_{w1}	Water Vapor Enthalpy at Prescrubber Inlet (kJ/kg; Btu/lb)
h_{w2}	Water Vapor Enthalpy at Absorber Exist (kJ/kg; Btu/lb)
K_A	Sum of Individual Pipe Fitting Loss Coefficients
L	Piping System Overall Length (m; ft)
L_c	Steam-Electric Unit Capacity Factor (Energy Generated/Capacity X Period)
m_w	Mass Addition of Make-Up Water Per Unit Mass of Dry Gas
m_{w1}	Mass Fraction of Water Vapor at Prescrubber Inlet (kg/kg; lb/lb-dry gas)
m_{w2}	Mass Fraction of Water Vapor at Absorber Exit (kg/kg; lb/lb-dry gas)
MW_P	Molecular Weight of Product P (kg/mole; lb/mole)
MW_R	Molecular Weight of Reagent R (kg/mole; lb/mole)
MW_{SO_2}	Sulfur Dioxide Molecular Weight (kg/mole; lb/mole)

NOMENCLATURE continued

P	Number of Chemical Products From Reactions With SO ₂
P _w	Pump or Fan Power Requirements (kW; hp)
R	Number of Reagents Reacting With SO ₂
S _R	Solubility of Reagent R (kg/l; lb/gal)
T ₁	Exhaust Gas Temperature at Prescrubber Inlet (°C; °F)
T ₂	Exhaust Gas Temperature at Absorber Exit (°C; °F)
t	Number of Hours Per Year
U	Unit Cost of Any Consumable (\$/unit)
\dot{V}_g	Exhaust Gas Volumetric Flow Rate (acmm; acfm)
V _L	Liquor Velocity (°C; °F)
\dot{W}	Flow Rate of Any Consumable (kg/hr; lb/hr)
\dot{W}_F	Fuel Flow Rate (kg/hr; lb/hr)
\dot{W}_L	Liquor Flow Rate (lpm; gpm)
\dot{W}_P	Product Mass Flow Rate (kg/min; lb/min)
\dot{W}_R	Reagent Mass Flow Rate (kg/min; lb/min)
\dot{W}_{SO_2}	Sulfur Dioxide Mass Flow Rate (kg/min; lb/min)
X _P	Product Concentration in Liquor (kg/l; lb/gal)
ΔP_{cv}	Control Valve Pressure Drop at Nominal Liquor Flow (nsc; psi)
ΔP_g	Exhaust Gas Pressure Loss (nsc; psi)
ΔP_L	Liquor Pressure Loss Through Piping System (nsc; psi)
ΔP_{sn}	Liquor Spray Nozzle or Distribution Header Pressure Loss (nsc; psi)
η_F	Fan Efficiency
η_H	Adiabatic Humidification Efficiency
η_P	Pump Efficiency
ν_R	Reagent Chemical Reaction Stoichiometric Coefficient (moles)
ν_P	Product Chemical Reaction Stoichiometric Coefficient (moles)
ν_{SO_2}	Sulfur Dioxide Chemical Reaction Stoichiometric Coefficient (moles)
ρ_L	Liquor Density (kg/M ³ ; lb/ft ³)
ρ_w	Density of Water (kg/l; lb/gal)

ABBREVIATIONS

acmm	actual cubic meters per minute
acfm	actual cubic feet per minute
C	Celsius
kJ	kilojoule
kWh	kilowatt hour
Btu	British thermal unit
F	Fahrenheit
Nsca	Newtons per square centimeter absolute
psia	pound per square inch absolute
molar	moles per liter
MW	megawatt
kg	kilogram
min	minute
lb/min	pound per minute
lbm/hr	pound-minute per hour
gpm	grams per minute
kg/hr	kilogram per hour
MBtu	mega-British thermal unit
in. vwc	inches of vertical water column
cm vwc	centimeter of vertical water column
kW/cm vwc	kilowatt per centimeter of vertical water column
hp/in. vwc	horsepower per inch of vertical water column
psi	pounds per square inch
lpm	liters per meter
Nsc	Newtons per square centimeter
kW	kilowatt
hp/psi	horsepower per pound per square inch
kW/psi	kilowatt per pound per square inch
m/s	meter per second
fps	feet per second

ABBREVIATIONS continued

m	meter
ft	foot
yr	year
hr	hour
moles/l	moles per liter
scf	seconds per cubic foot
vwc	vertical water column

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